(54) Title: FUEL CELL INCORPORATING NOVEL ION-CONDUCTING MEMBRANE
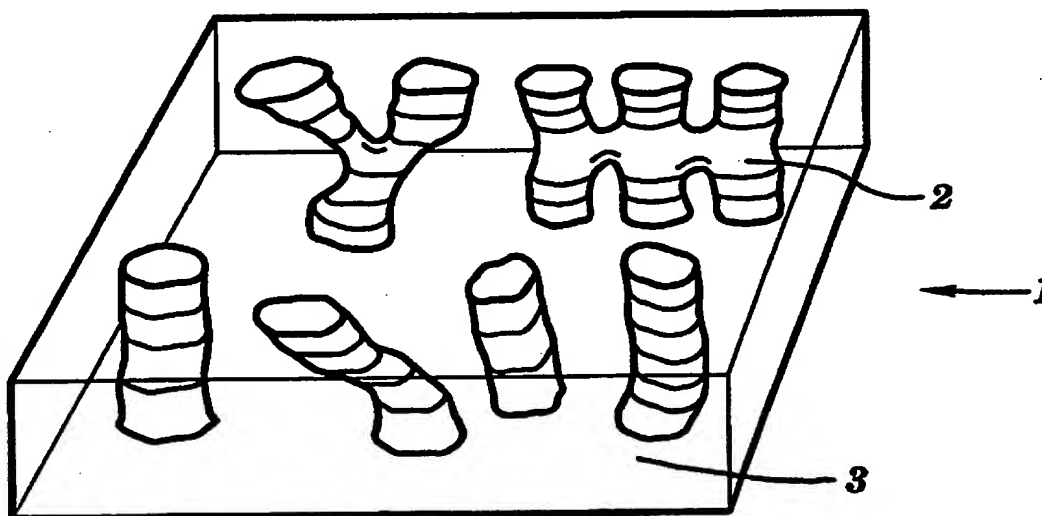
(57) Abstract

Fuel cells incorporating a novel ion-conducting membrane are disclosed. The membrane (1) comprises a plurality of acid-stable polymer molecules each having at least one ion-conducting component covalently bonded to at least one flexible connecting component. The membrane has ion-conducting components of the polymer molecules ordered such that a plurality of continuous ion-conducting channels (2) penetrate the membrane from a first face to a second face and such that the ion-conducting channels are situated in an elastic matrix (3) formed by the flexible connecting components. A preferred membrane is obtained by (a) sulfonating SEBS with sulfur trioxide under conditions that result in greater than 25 mol % sulfonation and (b) heating the polymer.

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FUEL CELL INCORPORATING NOVEL ION-CONDUCTING MEMBRANE

Field of the Invention

The present invention relates to fuel cells and in particular, to ion-conducting membranes for fuel
5   cells and to methods of constructing the same.

Background of the Invention

A fuel cell device generates electricity directly from a fuel source, such as hydrogen gas, and an oxidant, such as oxygen or air. Since the
10   process does not "burn" the fuel to produce heat, the thermodynamic limits on efficiency are much higher than normal power generation processes. In essence, the fuel cell consists of two catalytic electrodes separated by an ion-conducting membrane. The fuel
15   gas (e.g. hydrogen) is ionized on one electrode, and the hydrogen ions diffuse across the membrane to recombine with the oxygen ions on the surface of the other electrode. If current is not allowed to run from one electrode to the other, a potential gradient
20   is built up to stop the diffusion of the hydrogen ions. Allowing some current to flow from one electrode to the other through an external load produces power.

The membrane separating the electrodes must
25   allow the diffusion of ions from one electrode to the other, but must keep the fuel and oxidant gases apart. It must also prevent the flow of electrons. Diffusion or leakage of the fuel or oxidant gases across the membrane leads to explosions and other
30   undesirable consequences. If electrons can travel

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through the membrane, the device is fully or partially shorted out, and the useful power produced is eliminated or reduced.

5   It is therefore an object of this invention to produce a membrane which allows the diffusion of ions, but prevents both the flow of electrons and the diffusion of molecular gases. The membrane must also be mechanically stable.

10   In constructing a fuel cell, it is particularly advantageous that the catalytic electrodes be in intimate contact with the membrane material. This reduces the "contact resistance" that arises when the ions move from the catalytic electrode to the membrane and vice versa. Intimate contact can be

15   facilitated by incorporating the membrane material into the catalytic electrodes. [See Wilson and Gottsfeld J. Appl. Electrochem. 22, 1-7 (1992)] It is therefore an object of the invention to produce a membrane wherein such intimate contact is easily and

20   inexpensively made.

For reasons of chemical stability, fuel cells presently available typically use a fully fluorinated polymer such as Dupont Nafion° as the ion-conducting membrane. This polymer is very expensive to produce,

25   which raises the cost of fuel cells to a level that renders them commercially unattractive. It is therefore a further object of this invention to produce an inexpensive ion-conducting membrane.

Ion-conducting polymers are known. (See Vincent,

30   C.A., Polymer Electrolyte Reviews I, 1987). The known polymers are, for the most part, similar to

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sulfonated polystyrene because of the known ability
of sulfonated polystyrene to conduct ions.
Unfortunately, uncrosslinked, highly sulfonated
polystyrenes are unstable in the aqueous environment
5   of a fuel cell, and do not hold their dimensional
shape.

US Patent 4,849,311 discloses that a porous
polymer matrix may be impregnated with an ion-
conducting polymer to produce a fuel cell membrane.
10 However, the ion-conducting polymer must be dissolved
in a solvent which "wets" the porous polymer. When
the solvent evaporates, there is sufficient porosity
remaining in the porous polymer/ion-conducting
polymer composite material that molecular oxygen can
15 leak through to the fuel gas and result in an
explosion.

US Patent 3,577,357 (Winkler) discloses a water
purification membrane composed of block copolymers of
sulfonated polyvinyl arene block and alpha-olefin
20 elastomeric blocks. In one example a styrene-
isoprene-styrene triblock copolymer was selectively
hydrogenated, then sulfonated using a premixed
SO_3/triethylphosphate reagent at 60°C for 1.5 hrs. A
sulfonated styrene-(ethylene-propylene) copolymer was
25 the result. The method provided solid agglomerates
of the polymer which were rolled on a mill to remove
water, swelled in cyclohexane, slurried in an
isopropyl alcohol/water mixture, and coagulated in
hot water. No membrane was produced, and we have
30 found that polymers produced according to the method
of Winkler cannot be cast into films.

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Gray t al. [Macromolecules 21, 392-397 (1988)]
discloses a styrene-butadiene-styrene block copolymer
where the ion-conducting entity is a pendant short-
chain of poly(ethylene oxide) monomethyl ether (mPEG)
5   complexed with LiCF$_3$SO$_3$ salt and connected through a
succinate linkage to a flexible connecting entity
which is the butadiene block of the triblock
copolymer. The ion-conducting entity in the
butadiene block is in the continuous phase of the
10   polymer, and the areas populated by the ion-
conducting entities do not preferentially touch each
other to form continuous ion-conducting domains.
This morphology does not facilitate the ion-
conducting properties that are necessary for fuel
15   cell operation. The styrene block functions only as
a mechanical support structure for the polymer.
Moreover, the molecular design chosen by Gray et al.
is incompatible with the working environment of a
fuel cell. Because the succinate linkage which joins
20   the mPEG to the butadiene backbone and the ether
linkages which join the ethylene oxide units are
subject to cleavage by acid hydrolysis, these
linkages are unstable in the low pH environment of a
fuel cell even for short periods of time.

25   In the art of battery separators, as exemplified
by US Patent 5,091,275, a number of porous polymers
and filled polymer materials are known. The pores of
these polymers and composite materials are filled
with, typically, a liquid electrolyte to conduct ions
30   from one electrode to another in a battery. However,
these battery separator materials allow the passage
of gases, so that fuel cells made with them have an
unfortunate t ndency to explode as the oxygen leaks
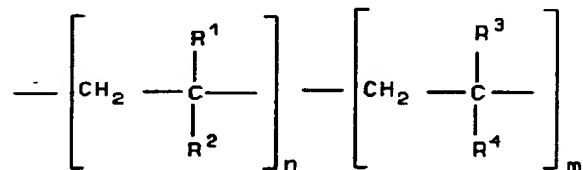into the hydrogen side of a fuel cell.

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Th re is therefore a need for an inexpensive, mechanically and chemically stable, ion-conducting membrane.

Summary of the Invention

5   In one aspect, the present invention relates to a membrane comprising a plurality of acid-stable polymer molecules each having at least one ion-conducting component covalently bonded to at least one flexible, rubbery connecting component. The

10   membrane has ion-conducting components of the polymer molecules ordered such that a plurality of continuous ion-conducting channels penetrate the membrane from a first face to a second face and such that the ion-conducting channels are situated in an elastic matrix

15   formed by the flexible connecting components. (See Fig. 1). Optimally, the channels have a cross-sectional dimension in the plane of the membrane of about 0.01 μm to 0.1 μm.

The flexible connecting component may be chosen

20   from the group

$$-\left[CH_2-\overset{\overset{\textstyle R^1}{|}}{\underset{\underset{\textstyle R^2}{|}}{C}}-\right]_n-\left[CH_2-\overset{\overset{\textstyle R^3}{|}}{\underset{\underset{\textstyle R^4}{|}}{C}}-\right]_m$$

and the group

$$\left[-CH_2CH=\overset{\overset{\textstyle R^5}{|}}{C}-CH_2-\right]_p$$

and the ion-conducting component may be chosen from
the group
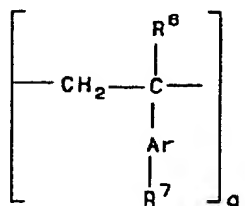
$$\left[-CH_2-\overset{\overset{\displaystyle R^6}{\displaystyle |}}{\underset{\underset{\displaystyle R^7}{\displaystyle |}}{\overset{\displaystyle |}{\underset{\displaystyle |}{C}}}}- \right]_q$$

wherein R^1, R^2, R^3 and R^4 are chosen independently from
the group consisting of hydrogen, phenyl and lower
5   alkyl;

    R^5 is hydrogen, chlorine or lower alkyl;

    R^6 is hydrogen or methyl;

    R^7 is $-SO_3H$, $-P(O)(OR^8)OH$, $-R^9-SO_3H$ or $-R^9-$
$P(O)(OR^8)OH$ where R^8 is hydrogen or lower alkyl and R^9
10   is lower alkylene;

    Ar is phenyl; and

    m, n, p and q are zero or integers from 50 to
10,000.
The terms lower alkyl and lower alkylene include
15   hydrocarbons having from 1 to 6 carbons in linear,
branched or cyclic structure.

    In a preferred embodiment the flexible
connecting component is chosen from the group
consisting of poly(alpha-olefins), polydienes, and
20   hydrogenated derivatives of polydienes, and the ion-
conducting domain is provided by a component chosen
from the group consisting of the sulfonic acids of
polystyrene and poly(α-methylstyrene). Most
preferably, the flexible connecting component is
25   chosen from the group consisting of poly(ethylene-
butylene) and poly(ethylene-propylene) and sulfonate
or sulfoxide crosslinking occurs betw n the
polystyrene or poly(α-methylstyrene) components.

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Another useful membrane is an acrylonitrile-
butadiene-styrene terpolymer (ABS), the styrene
component of which is sulfonated.

Because the precise structure of a preferred
5   membrane of the invention is difficult to
characterize, it may alternatively be described as a
highly sulfonated polymeric membrane produced by the
process of:
        (a)   adding a 3-4 wt% solution containing
10   3.6 equivalents of styrene-(ethylene-butylene)-
styrene triblock copolymer in 80/20
dichloroethane/cyclohexane and a 3-4 wt% solution
containing about 3.6 equivalents of sulfur trioxide
in dichloroethane to a 0.6 wt% solution containing
15   about one equivalent of triethylphosphate in
dichloroethane at -5° to 0° C;
        (b)   stirring for 15 to 30 minutes at -5°
to 0° C, and then room temperature for 8 to 14 hours;
        (c)   heating at about 80° C for 30 to 40
20   minutes until a purple color is evident;
        (d)   evaporating the dichloroethane and
cyclohexane at 40° C to obtain a viscous purple
liquid;
        (e)   resuspending the viscous purple liquid
25   to form a fine dispersion of 8 to 10 wt% in 80/20
dichloroethane/cyclohexane; and
        (f)   casting the dispersion on a substrate
to form a membrane. The membrane so formed absorbs
at least 50% of its weight in water and in its fully
30   hydrated state can be stretched to at least 100% of
its original dimension without fracture. It exhibits
a conductivity of at least 10^{-5} S/cm in its fully
hydrated state.

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The styrene-(ethylene-butylene)-styrene triblock copolymer which forms the substrate for the process described above may have a number average molecular weight of about 50,000 and styrene units may comprise
5   about 20 to 35 wt% of the triblock copolymer. Preferably, the membrane is more than 25 mol% sulfonated.

In another aspect, the invention relates to a fuel cell comprising: (a) the membrane described
10   above; (b) first and second opposed electrodes in contact with the membrane; (c) means for supplying a fuel to the first electrode; and (d) means for permitting an oxidant to contact the second electrode.

15   In one embodiment, one of the electrodes is composed of catalytic particles and the membrane functions as a binder for the electrode. In other embodiments, both electrodes may be composed of catalytic particles and the membrane functions as a
20   binder for both electrodes.

In a related aspect the invention relates to an electrolysis cell having the same structure as the fuel cell above.

In a further aspect, the invention relates to a
25   process for preparing a mechanically stable, ion-conducting membrane comprising the steps of:
            (a)   adding a solution containing 3.6 equivalents of a styrene-containing block copolymer in an appropriate solvent and a solution containing
30   about 0.9 to 3.6 equivalents of sulfur trioxide in an appropriate solvent to a solution containing from

about 0.3 to about 1.2 equivalents of
triethylphosphate in an appropriate solvent at -5° to
0° C;

        (b) stirring for 15 to 30 minutes at -5°
to 0° C, and then room temperature for 8 to 14 hours;

        (c) heating at about 80° C until a color
change occurs;

        (d) evaporating the solvent to provide a
residue;

        (e) resuspending the residue to form a
fine dispersion in a suspending solvent; and

        (f) casting the dispersion on a substrate
to form a mechanically stable, ion-conducting
membrane.

As before, a preferred styrene-containing
polymer is a styrene-(ethylene-butylene)-styrene
triblock copolymer having a number average molecular
weight of 50,000 wherein styrene units comprise
about 30 to 35 wt% of the triblock copolymer.
Preferably, the membrane is more than 25 mol%
sulfonated.

In a particular embodiment, the process
comprises:

        (a) adding a 3-4 wt% solution containing
3.6 equivalents of styrene-(ethylene-butylene)-
styrene triblock copolymer in 80/20
dichloroethane/cyclohexane and a 3-4 wt% solution
containing about 3.6 equivalents of sulfur trioxide
in dichloroethane to a 0.6 wt% solution containing
about one equivalent of triethylphosphate in
dichloroethane at -5° to 0° C;

        (b) stirring for 15 to 30 minutes at -5°
to 0° C, and then room temperature for 8 to 14 hours;

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    (c) heating at about 80° C for 30 to 40 minutes until a purple color is evident;

    (d) evaporating the dichloroethane and cyclohexane at 40° C to obtain a viscous purple

5 liquid;

    (e) resuspending the viscous purple liquid to form a fine dispersion of 8 to 10 wt% in 80/20 dichloroethane/cyclohexane; and

    (f) casting the dispersion on a substrate

10 to form a membrane.

   In a further aspect, the invention relates to a process for preparing a sulfonic acid ionomer of a styrene-(ethylene-butylene)-styrene triblock copolymer (SEBS), the improvement which comprises

15 using a sulfur trioxide-triethylphosphate complex that is formed in the presence of the SEBS, whereby the SEBS is not less than 25 mol% sulfonated.

Brief Description of the Drawings

   Fig. 1 is an idealized perspective view of a

20 membrane according to the invention.

   Fig. 2 is a schematic diagram of a typical fuel cell incorporating a membrane of the invention.

Detailed Description Including Preferred Embodiments

   The ion-conductive polymer membrane of the

25 invention is shown in Fig. 1 in schematic form. The membrane 1 is a multicomponent polymer composed of at least one ion-conducting component which is covalently bonded to at least one flexible component.

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The minimum requirements for the ion-conducting
component are that the ionic grouping (e.g. sulfonic
or phosphonic acids) be a strong enough acid to
provide sufficient dissociation of charge carriers
5   (protons) in an aqueous environment, possess moderate
temperature stability (up to at least 40°C), and
sufficient number of such groupings be present to
potentially form a network of interconnected domains
2, which extends throughout the membrane 1 forming an
10   ion conduction pathway from one side to the other
side of the membrane.

The minimum requirements for a flexible
connecting component are that the main chain of the
grouping possess sufficient mobility at the operating
15   temperature of the fuel cell to facilitate
reorganization of the ionically conducting component
into a domain to which it is connected, and to be
insoluble in the aqueous environment of a fuel cell.
The domains 3 formed by the flexible connecting
20   components should be amorphous or at least partially
amorphous at the operating temperature of the fuel
cell.

There are a number of ways of connecting polymer
components which can result in useful ionically
25   conducting membranes.

In this invention, a sulfonated styrene -
(ethylene-butylene) triblock copolymer (example 3)
was considered the most preferred embodiment because
of the superior mechanical properties that this
30   arrangement possess s. However, other topological
arrangem nts are possible.

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For multicompon nt polymers, the repeating units
of each of the components can be connected in
different sequences depending on the method of
synthesis. The A and B units are connected in a
sequence by covalent bonds such that the expression
$[(A)_n(B)_m]p$, describes the polymer microstructure. If
n units of A are covalently bonded to m units of B in
sequences (p is arbitrary) where the stochastic
process followed is Bernoullian (or zero-order
Markov) then the polymer is a called a random
copolymer. (The stochastic process followed depends
on the relative reactivities of the two monomers in
the copolymerization; see Odian, G., Principles of
Polymerization, 1992.) However, if the stochastic
process which the sequence of A and B units follow is
not Bernoullian (e.g. terminal model or first-order
Markov) then polymer is called a statistical
copolymer.

Limiting cases exist for which the relative
reactivities of the two monomers (A prefers to add B
and B prefers to add A) result in the sequence -AB-
to be repeated p times (for m=n) and this is called
an alternating copolymer.

A second limiting case exists where (A prefers
to add A and B prefers to add A until A is consumed,
then B is added) the polymer is composed of two
components, A and B, and n units of A are covalently
bonded at one junction point (p=1) to m units of B,
then each of these sequences of component s is called
a block and the polymer is called a diblock
copolym r. Similarly, if a third block of n units of
A is bonded at a second junction point (p=2) on the
B-block, then the polymer is called a triblock

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copolymer (and equivalently if a third block of m
units of B is bonded to A).

If a sequence of m units of B are bonded to a
sequence of n units A at one or more branch points
5   (p ≥ 1) along the sequence of m units of B then the
polymer is called a graft (or graft-block, for p=1)
copolymer.

Multi-block polymers, where p is the number of
junction points for p+1 blocks, can also be
10   envisioned as well as the less common star-block
copolymers, where p is the number arms connected at
one or more branch points.

Combinations of these types (e.g.
statistical/block or statistical/graft) are also
15   possible. Random, statistical and combination
terpolymers are polymers which possess three unique
units in the microstructure. An example is
acrylonitrile-butadiene-styrene terpolymer where the
butadiene or styrene-butadiene units compose the main
20   chain and at various branch points a statistical
arrangement of styrene and acrylonitrile units are
positioned (i.e. statistical/graft).

A preferred embodiment of this invention is a
graft copolymer of sulfonated styrene and butadiene
25   where the sulfonated styrene block is covalently
bonded to the butadiene block (or sulfonated styrene-
butadiene sequence) at one or more branch points
along the butadiene chain.

Another preferred embodiment of this invention
30   is the combination statistical/graft of

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acrylonitrile-butadiene-sulfonated styrene
terpolymer. A more preferred embodiment is the
hydrogenated butadiene analog of each of the
forementioned preferred embodiments.

5   The sulfonation of the styrene units of each of
these topological arrangements can be achieved by the
synthetic method described below. The introduction of
sulfonate groups onto polystyrene is known. Early
methods involved heating the polymer in sulfuric acid
10   for hours; an improved method employs silver sulfate
added to the sulfuric acid as a catalyst. More
recently, complexes with a number of agents such as
phosphorus pentoxide, triethyl phosphate and tris (2-
ethylhexyl) phosphate have been used to modulate the
15   reactivity of sulfur trioxide. Acyl sulfates, formed
by premixing, include sulfuric acid/acetic anhydride,
sulfur trioxide/acetic acid, sulfur trioxide/lauric
acid, and chlorosulfonic acid/lauric acid. It has
been suggested that the reduced reactivity of acyl
20   sulfates results in better sulfonation control than
was observed in previous methods with virtually no
crosslinking. In addition, chlorosulfonic acid and
trimethylsilyl-sulfonyl chloride have been found
useful. Each requires hydrolysis to obtain the
25   desired sulfonic acid. All of the above processes
are conveniently carried out in chlorinated solvents
(e.g. 1,2-dichloroethane, trichlorobenzene, methylene
chloride, etc.) However, hydrocarbon solvents have
been used with some success (e.g. cyclohexane).

30   Methylene units are readily inserted between the
sulfonate group and the phenyl group by first
carrying out an acylation of the ring with an α, ω-
acyl/alkyl dichloride f desired carbon length and

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then transforming the chloride into the sulfonate.
Polymers having improved temperature stability can
often be obtained by the insertion of the methylene
unit.

5   A unique route to sulfonated polymers is the use
of sulfur dioxide and chlorine gases to
chlorosulfonate polymers such as polyethylene. Again,
the procedure requires hydrolysis to obtain the
protonic form of the polymer.

10   Alternatively, it is possible to first sulfonate
the monomers then to carry out the polymerization.
The sulfonated monomers (protonic form) are sometimes
polymerized in the sodium salt form or can be
protected by forming the sulfonyl ester then
15   polymerized. Ion exchange or hydrolysis follows to
obtain the protonic form of the polymer.

Although less known, the phosphonation of
polystyrene is also a viable route to ion-conducting
groups. Phosphonic acid groups and alkyl substituted
20   phosphonic acid groups may be introduced onto the
polymer by alkylation with the corresponding
chloroalkyl phosphonates or phosphonation with alkyl
phosphites.

For the purpose of this invention, possible ion-
25   conducting groups include $-SO_3H$ and $P(O)(OR^8)OH$
wherein R^8 is hydrogen or lower alkyl.

The most preferred ionic conducting groups are
poly(styrene sulfonic acid) and p ly(alpha-methyl
styrene sulfonic acid). Poly(styrene sulfonic acid)
30   and poly(alpha-m thyl styrene sulfonic acid) may be
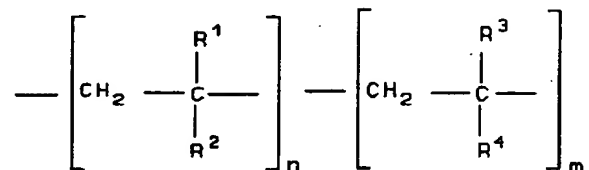
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analogously prepared and used.

The flexibility of a block or sequence of units which is covalently bonded to an ion-conducting group is an important object of this invention. Chain
5   flexibility is associated with the glass transition temperature of the polymer, block or characteristic sequence of units. The glass transition temperature (or Tg) is the temperature at which large scale (translational and rotational) molecular motion of
10   chains begins. Thus, it follows that above the glass transition temperature (i.e. Tg+50) the chains possess more mobility than below Tg (i.e. Tg-50). The Tg of a polymer is largely a function of the bonding, the nature of the atoms in the chain, the secondary
15   forces, the chain substitution and chain connectivity.

The melting temperature of a chain-folded crystallite, T_m has an effect on the chain flexibility. Because chains which crystallize are
20   tied up in the crystalline regions, these have considerably less mobility. A good approximation for a linear hydrocarbon polymer is that the Tg is 2/3 the value of its Tm.

The crystallization of polymer chains can be
25   reduced or eliminated by incorporating a nonsymmetrical (or symmetry-breaking) unit into the chain structure (e.g. introducing butylene units into polyethylene to give rise to ethylene-butylene polymers). This process has the effect of reducing
30   crystallinity and increasing flexibility. For simplicity, Tg is used as a measure of chain flexibility.

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Preferred flexible connecting groups of
saturated origin are described by the formula,

$$-\left[CH_2-\overset{\overset{\displaystyle R^1}{|}}{\underset{\underset{\displaystyle R^2}{|}}{C}}-\right]_n-\left[CH_2-\overset{\overset{\displaystyle R^3}{|}}{\underset{\underset{\displaystyle R^4}{|}}{C}}-\right]_m$$

wherein R^1, R^2, R^3 and R^4 are independently hydrogen or
lower alkyl. When R^1, R^2 and R^3 are hydrogen and R^4 is

5   n-butyl, then the structure is ethylene-butylene.

The most preferred embodiment of the flexible
connecting group is ethylene-butylene. The next most
preferred is when the flexible connecting group is
ethylene-propylene. The preparation of ethylene-

10   butylene and ethylene-propylene are well known in the
art.

Preferred flexible connecting groups of
unsaturated origin are described by the formula,

$$\left[-CH_2CH=\overset{\overset{\displaystyle R^5}{|}}{C}-CH_2-\right]_p$$
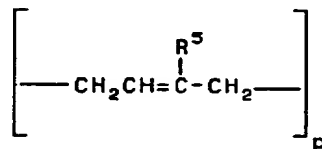
15   wherein R^5 is hydrogen, chlorine or lower alkyl. When
R^5 is H, the structure is poly(1,4-butadiene); when R^5
is Cl, the structure is poly(chloroprene); and when R^5
is methyl, the structure is poly(1,4-isopr ne). The
preparation of poly(butadiene), poly(isoprene),

20   poly(chloroprene) and their isomers are well known in

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the art.

The 1,2 isomers of polymers are also included in this set of unsaturated origin (with 1,4 isomers). It should be noted that different amounts of 1,2 isomers
5   will be present in the 1,4 isomers depending on the catalyst used in the polymerization.

The molecular weight of the polymer should be preferably no less than 10,000 g/mol and most preferably be greater than 50,000 g/mol for adequate
10   mechanical strength. A membrane thickness of 25-1000 μm, preferably 100-500 μm and most preferably 250-350 μm provides sufficient mechanical integrity to produce free-standing, useful membranes with enough ion-conductivity to cause acceptably low voltage
15   drops under working conditions.

As measured by ac impedance analysis, the room temperature ionic conductivity of the fully hydrated membranes must be at least 10^{-6}, preferably at least 10^{-4} and most preferably at least 10^{-2} S/cm. The
20   electronic resistivity due to electron flow must be at least 10^2, preferably at least 10^4 and most preferably at least 10^6 Ohm-cm.

As measured by analytical weight uptake measurements, the membranes should absorb between 10
25   and 150%, preferably between 30 and 100%, and most preferably between 50 and 80% water by weight. In the fully hydrated state, membranes can be stretched at least 10%, preferably 25%, and most preferably at least 50% of th ir original length.

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The g n ral requirements needed for a copolymer
film to function well as fuel cell membrane are that
the copolymer possess a flexible connecting
component, such as a hydrogenated butadiene unit and
5   an ion-conducting component. These two units must
occur in the polymer, such as a sulfonated styrene
unit, in such a way that the morphological structure
of the polymer can give rise to a plurality of low
resistance, ion transport pathways. The pathways are
10   composed of a plurality of touching ion-conducting
domains which are presumed to be elongated and
organized into a cylindrical or channel type
structure. A limited number of copolymers can be
envisioned which can exhibit these types of
15   structures.

Commercially available styrene-diene and
styrene-hydrogenated diene triblock copolymers
(Shell) are preferred membrane materials. The styrene
content of between 28-31 wt% provides domains of
20   elongated cylindrical morphology when cast from the
appropriate solvent. The cylinders of polystyrene are
apparently retained after sulfonation. These
cylindrical domains of the styrene material are
aligned parallel to each other in a grainy structure,
25   each domain being separated by a layer of the
elastomeric material which connects adjacent domains
together.

Such a mixture of cylindrical conducting
material, each cylinder separated from the next by a
30   non-conducting material, would be expected to be non-
conducting. We have found however, that when the
material is sulfonated, and when it is then hydrated,
that the sulfonated polystyrene domains swell and

presumably punch through the surrounding elastic
material to allow contact between neighboring
cylinders. This contact presumably connects the
aligned cylinders to each other end to end, and the
5   conductivity is higher than that which one would
expect from normal percolation models.

Diblock copolymers that can exhibit cylindrical
domains can also be obtained commercially. Although
they do not take advantage of the interconnected
10   morphology of triblock copolymers, the insolubility
of the hydrogenated butadiene units may be enough
impart the required amount of mechanical integrity
for fuel cell membranes. These can be hydrogenated
using conventional methods (Wilkinson's catalyst)
15   known to those skilled in the art. They may be
sulfonated as easily as their triblock copolymer
counterparts.

Graft copolymers are also available commercially
or they may be isolated from commercial polymer
20   resins. An example is high impact polystyrene (HIPS)
which has a graft copolymer content of about 15% by
weight. The grafted part may be extracted with an
acetone-methyl ethyl ketone mixture. Similar
transformation reactions can lead to a sulfonated
25   styrene-hydrogenated butadiene copolymer. These can
also exhibit morphologies possessing channels.

Controlled monomer feed conditions can provide
random or statistical copolymers which possess
chemical microstructures with various degrees of
30   'blockiness', where short sequences of styrene units
are obtained. Segregated network type structures may
then be possible. However, such substrates are

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inferior to those described above. A statistical
copolymer of styrene-hydrogenated butadiene rubber
when sulfonated may be capable of organizing into
channels.

5   The exploitation of elastomers such as
acrylonitrile-butadiene-styrene (ABS), acrylonitrile-
chlorinated ethylene-styrene (ACS) and ethylene-
propylene-diene (EPDM) polymers may also be possible,
if the morphologies of these polymers are capable of
10   organizing into channels after sulfonation. ABS,
which is a butadiene backbone with a statistical
copolymer of acrylonitrile-styrene grafted onto it,
may exhibit channels after selective hydrogenation of
butadiene followed by sulfonation of the styrene
15   units.

        A mixture of block copolymer and the hompolymer
could also be used. At low percentages of the
homopolymer, the block copolymer would determine the
morphology of the material.

20   ACS is similar in preparation to ABS. It is
prepared by partial dehydrohalogenation of
chlorinated polyethylene leading to double bonds
which can be subsequently reacted to produce
acrylonitrile-styrene grafts; the styrene units are
25   then sulfonated. Channels may be possible at a
critical styrene composition.

        Ethylene-propylene-diene, the diene usually
being hexadiene, may be sulfonated using methods
described herein. At a critical composition of the
30   dien , a channel structure may be possible.

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EXAMPLES

The fuel cell assembly used in all experiments
was a low pressure clamping cell, an electrochemical
test stand was used for collecting data and porous
5   carbon catalyst electrodes (20% Pt on carbon) were
all obtained from Electrochem, Inc., Woburn, MA. The
carbon electrodes had a platinum loading of 1 mg/cm^2
of flat area and Nafion 117 was used as the binder
(see Gottesfeld, S. and Wilson, M.S., J. Appl.
10   Electrochem., 22, 1, 1992). Commercial hydrogen and
oxygen gases were used without pressurization or

humidification. The experiments were carried out at
room temperature (23°C).

The ionic conductivity measurements were carried
15   out with a 1260 impedance analyzer from Schlumberger
Instruments, Inc., Burlington, MA. A hydrated film
was inserted between the two blocking electrodes of a
spring-loaded cell. A 5 mV ac voltage was applied.
The frequency range of the experiment was 50 mHz to 1
20   MHz. The method is similar to that described by
Vincent, C.A., Polymer Electrolyte Reviews I, 1987.
Conditions and equipment in the subsequent examples
are those described here except where specified.

Example 1
25   Fuel Cell Performance of Nafion 117 (Comparative)

The Nafion 117 membrane was obtained from Dupont,
Wilmington, DE and was used as received. After one
w ek of immersion in distilled water, the ionic
conductivity of the membran was measured to be 5 x
30   10-7 S/cm. In a typical experiment Nafion was hot

pressed between two porous carbon catalyst electrodes
(Electrochem Inc., Woburn, MA) using low pressure.
The carbon electrodes had a platinum loading of
1 mg/cm^2 of flat area and incorporated Nafion 117. The
5   Nafion membrane was immersed in distilled water for
thirty minutes prior to testing. The fuel cell
produced 5mA/cm^2 at 400 mV for a short period of time
(ca. 10 min.). However, a steady drop in current and
voltage was observed over the next 25 minute period
10   as the membrane dried out. After this time, the cell
was completely dried out with zero current and
voltage. Frequently, after the cell was disassembled
to check for water retention, it was found that the
electrodes had separated from the membrane.

15   Example 2
     Preparation and Testing of an Ionically Conductive,
     Sol-Gel Impregnated, Microporous Polyethylene
     Membrane (Comparative)

     1.   The Sol-Gel Formulation: To a dry 250 ml beaker
20   fitted with a magnetic stir bar, 8.68 grams (0.042
     mol) of tetraethoxysilane was added. While stirring
     51.76 grams (0.215 mol) of phenyltriethoxysilane
     (PTES) was added, and 11.50 grams (0.25 mol) of
     absolute ethanol. Next 17.5 grams (0.28 mol) of
25   concentrated nitric acid (70.6% by weight) was added
     dropwise over the course of about 15 minutes. A
     clear, low viscosity liquid was obtained.

     2.   Impregnation of Microporous Polyethylene
     Membranes (Evanite Fiber Corporation, Corvalis, OR):
30   Enough of the liquid was poured into a shallow, glass
     vessel (e.g. watch glass) to a d pth of about 5 mm.
     Membranes (2 in. x 2 in.) were immersed into the

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liquid. The membranes were allowed to soak until the
solution completely permeated them. Next, the
membranes were turned over in the vessel to ensure
homogeneous infiltration of the liquid. The membranes
5   were allowed to soak for 2-3 minutes. The membranes
were removed, placed on a Teflon° sheet for several
minutes to remove excess liquid, then hung on clip
for 8 hours to cure. In one case, sulfonated PTES
(see step 4) was used at this stage instead of
10   sulfonating (in step 3) after impregnation.

3.   Sulfonation of the Silane Impregnated Membranes:
Sulfonation was carried out by immersing the silane
impregnated membrane into hot, concentrated sulfuric
acid (97% by weight) at 60-70°C. The residual acid was
15   remove by immersing the sulfonated membranes into
distilled water. The degree of sulfonation was
controlled by the time of immersion in the sulfuric
acid (ca. 30 min.).

4.   Sulfonation of Phenyltriethoxysilane (PTES):
20   About 14.94 grams (0.108 mol) of triethyl phosphate-
sulfur trioxide complex (1:3) was dissolved in 100 ml
of dry methylene chloride and the solution was
carefully added to a graduated addition funnel. To a
dry 250 ml 3 neck round bottom flask fitted with a
25   condenser, argon purge line and addition funnel,
25.88 grams (0.108 mol) of PTES and 25 ml of
methylene chloride were added. The reactor was cooled
to -4 to -2°C. The SO_3 solution was slowly fed to the
reactor while keeping the reaction temperature < -2°C.
30   Upon completion of the addition, the reaction
temperature was h ld at < -2°C for thirty minutes.
Next, the reactor was allow d to com to r om
temperature (~23°C). Most of the solvent was vacuum

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stripped from the sulfonated PTES. Alternatively, a
similar compound 2-(4-chlorosulfonylphenyl)
ethyltrimethoxysilane (Huls, Piscataway, NJ) was used
in place of sulfonated PTES. The acid was produced
5   by immersing the cured membranes in boiling water.

5.   Experimental Results: The membranes were
immersed in distilled water, shaken dry of adherent
water and sandwiched between two porous platinum wire
electrodes . The sulfonated membranes gave stable
10   current (ca. 50 mV at 4 mA/cm^2) for approximately 30
minutes. After this time, the current began to fall
precipitously, because of excessive oxygen/hydrogen
gas leakage. In more than a few experiments, oxygen
and hydrogen reacted explosively, emitting puffs of
15   smoke from the hydrogen gas outlet port, resulting in
a unsightly hole in the membrane.

Example 3
The Preparation and Testing of Sulfonated Styrene-
(Ethylene-Butylene)-Sulfonated Styrene Triblock
20   Copolymer

1.   Preparation of Sulfonated Styrene-(ethylene-
butylene) Triblock Copolymer: The styrene-(ethylene-
butylene)-styrene triblock copolymer (SEBS) was
obtained from Shell Chemical Co., Lisle, IL under the
25   tradename Kraton°. A 3.8 wt% solution of the SEBS
copolymer was prepared in a solvent mixture having a
composition of 80 wt% 1,2-dichloroethane (DCE) and 20
wt% cyclohexane. The dissolution sequence was as
follows: About 10 grams (0.03 mol, 3.1 grams
30   styr ne) of the triblock copolymer was added to 200
grams of DCE and allowed to mix for 2-4 hours. A
cloudy emulsion was obtained. Warming the soluti n

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favored th formation of a slightly tinted polymer microemulsion. About 53 grams of cyclohexane was added and after stirring for a few minutes a clear solution was obtained. The polymer solution was
5   transferred to a 500 mL dropping funnel.

Sulfur trioxide (SO_3) was weighed out into a glass vessel while in an inert gas glove bag. A 3.4 wt% solution of SO_3 in DCE was prepared. About 2.34 grams (0.03 mol) of SO_3 (bp 17°C) was dissolved in 66
10   grams of DCE. The solution was transferred to an appropriate dropping funnel.

A resin kettle (reactor) was fitted with an electric motor using a variable transformer, a paddle, an argon gas inlet/outlet, oil bubbler, two
15   Claissen adaptors, and the two dropping funnels. The reactor was charged with 262 grams of DCE and 1.5 grams (0.0082 mol, 3.6:1 SO_3) of triethyl phosphate (TEP). Vigorous agitation and inert gas purge was begun and the reactor was cooled to -2°C in an
20   ice/ethanol Dewar. The SO_3 and polymer solutions were added alternately dropwise to the reactor in small aliquots. The aliquot size (e.g. 4-5 ml for SO_3) was roughly 1/12 the total volume of each of the solutions. The aliquots were added slowly, over the
25   course of 5 minutes for the SO_3 and over the course of 5-10 minutes for the polymer. A rapid inert gas stream, a temperature range of -5 to 0°C (-2°C nominal), and vigorous stirring were maintained throughout the course of the reaction. After all of
30   the aliquots for each of the solutions had been added, the reaction was left stirring at low temperature for between 15 and 20 minutes. At the end of this period the extraneous glassware was

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removed, the orifices were capped, and the paddle
assembly was replaced with a stir bar and a magnetic
stirrer. The reactor was allowed to stir overnight
and warm up to room temperature (20-25°C).

5   The mixture was filtered through coarse filter
paper. The liquid (filtrant) was transferred to a
beaker and heated to boiling on a hot plate until a
distinct purple color was apparent (after about 30-40
minutes). The solution was concentrated on a rotary
10   evaporator at 40°C and partial vacuum until a viscous
purple liquid was obtained. Next, the viscous liquid
was resuspended in about 62 grams (enough for a 3-5
wt% solution) of DCE. The DCE was allowed to
evaporate until undissolved gel was formed on the
15   walls of the container (about 8-10 wt% solution).
The liquid was decanted and enough cyclohexane was
added to dissolve a large portion of the undissolved
gel. The two solutions were mixed and concentrated
by evaporation (roughly 80% DCE) until a fine
20   dispersion of the polymer was obtained.

        This dispersion was cast onto Teflon° and onto
aluminum substrates to form a highly conducting
membrane. The membrane absorbs at least 50% of its
weight in water. The film could be stretched as much
25   as 100% of its original length. As measured by ac
impedance analysis, the room temperature, dc
conductivity of the fully hydrated film was no less
than 10^{-5} S/cm.

        The polymer was 50 mol% sulfonic acid based on
30   the styren content fr m titration, and the solution
was heated to boiling and held until it turned a r d-
purple color.

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There are two features of the foregoing process
that appear important to producing useful polymers:
(1) sulfonating to high sulfonate levels, and (2)
heating the sulfonation mixture after sulfonation.
5   Heating of the sulfonation reaction solution is
necessary for the formation of a viscous dispersion
(5-10% solids) which can be cast into films. The
dispersion is not formed unless heated and only after
a red-purple solution is obtained. It is believed
10   that the heating step may cause decomposition of
sulfonate groups and/or crosslinking through sulfone
or sulfonyl ester linkages, although applicants do
not wish to be held to this theory.

The process of the invention provides a film
15   which is sulfonated to a level of 53 mol%. This level
of sulfonation is attainable in about 1.5 hrs at -3°C.
In the procedure of Winkler (US Patent 3,577,357),
the sulfonation was also carried out for 1.5 hrs but
at 60°C. However, as described in a comparative
20   example in US Patent 5,239,010, the procedure of
Winkler results in a polymer with only 10 mol%
sulfonation. The water adsorption of such a film
would be about 5%. This would indicate that even if
Winkler's polymer could be cast, it would probably
25   not function well as an ion-conducting membrane.

2.   Fuel cell Performance of Sulfonated SEBS: The
membrane was immersed in distilled water, shaken dry
of adherent water and sandwiched between two porous
carbon catalyst electrodes. Initially, the fuel cell
30   produced 50 mA/cm^2 at 400 mV and continued to improve.
After 72 hours the current climbed to 115 mA/cm^2 at
450 mV.

Th same features of the membrane that lend

themselves to its use in fabricating fuel cells also
render it suitable for use in fabricating an
electrolysis cell for electrolyzing water to hydrogen
and oxygen. The electrode processes that occurred in

5   the fuel cell to produce electrical energy and water
by consuming hydrogen and oxygen can be reversed to
consume energy and produce hydrogen and oxygen from
water. A voltage is applied across the cell to
oxidize water to oxygen and protons, and the protons

10   are allowed to pass through the membrane to the
cathode, where they are reduced with concomitant
production of hydrogen gas. Water is continuously
supplied to the anode, and hydrogen and oxygen are
drawn off the cathode and anode respectively. The

15   most immediate utility of such a cell is as a power
storage device wherein the hydrogen and oxygen so
produced are stored and reused to power the fuel cell
upon demand.

A typical cell is shown in Fig. 2. It comprises

20   an ion-conducting membrane 10, a catalyst electrode
11, current collector 12 and oxidant manifold 13. On
the opposite side of the membrane 10 are a second
catalyst electrode 16, a second current collector 17,
and a fuel manifold 14.

25   Its operation as a fuel cell is described as
follows with hydrogen as the fuel, but any oxidizable
fuel could be used. Hydrogen is fed into the fuel
manifold 14. Hydrogen reacts with catalyst electrode
16 to form protons. The electrons which are formed

30   by the interaction of the hydrogen and catalyst in
the hydrogen electrode are collected by the hydrogen
curr nt collector 17 and fed into the external
electrical load 15. The protons are absorbed by the

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ion-conducting membrane **10**. Oxygen is fed into the
oxidant manifold **13**. The oxygen reacts with the
catalyst in the oxygen electrode and the electrons
returning from the external electrical load **15**
5   through the oxygen current collector **12** to form
oxygen radicals within the catalyst electrode **11**.
Protons from the ion-conducting membrane **10** seek out
the oxygen radicals driven by the electrical
potential created by the formation of the oxygen
10   radicals. Protons combine with the oxygen radicals
to form water in the oxygen electrode completing the
electro-chemical circuit. The water is released by
the electrode **11** and removed from the cell through
the manifold **12**.

15   While the invention has been particularly shown
and described with reference to preferred embodiments
thereof, it will be understood by those skilled in
the art that other changes in form and details may be
made therein without departing from the spirit and
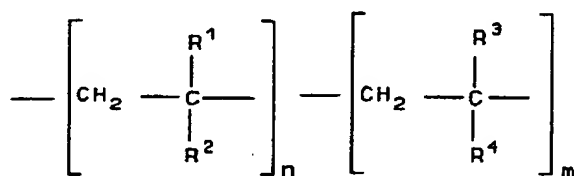20   scope of the invention.
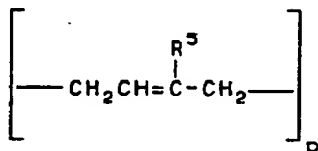
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We claim:

    1.   A membrane comprising a plurality of acid-stable polymer molecules each having at least one ion-conducting component covalently bonded to at least one flexible connecting component, said

5   membrane having ion-conducting components of said polymer molecules ordered such that a plurality of continuous ion-conducting channels penetrate the membrane from a first face to a second face and such that said ion-conducting channels are situated in an

10   elastic matrix formed by said flexible connecting components.

    2.   The membrane of claim 1 wherein said channels have a cross-sectional dimension in the plane of the membrane of about 0.01 μm to 0.1 μm.

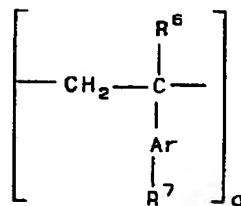   3.   The membrane of claim 1, wherein the flexible connecting component is chosen from the group

$$-\left[CH_2-\overset{\displaystyle R^1}{\underset{\displaystyle R^2}{\overset{|}{\underset{|}{C}}}}-\right]_n-\left[CH_2-\overset{\displaystyle R^3}{\underset{\displaystyle R^4}{\overset{|}{\underset{|}{C}}}}-\right]_m$$

5   and the group

$$\left[-CH_2CH=\overset{\displaystyle R^5}{\overset{|}{C}}-CH_2-\right]_p$$

and wherein the ionic conducting component is chosen from the group

$$\left[-CH_2-\overset{\overset{\displaystyle R^6}{|}}{\underset{\underset{\displaystyle R^7}{|}}{\underset{|}{C}}}- \right]_q$$

wherein R^1, R^2, R^3 and R^4 are chosen independently from the group consisting of hydrogen, phenyl and lower alkyl;

R^5 is hydrogen, chlorine or lower alkyl;

R^6 is hydrogen or methyl;

R^7 is $-SO_3H$, $-P(O)(OR^8)OH$, $-R^9-SO_3H$ or $-R^9-P(O)(OR^8)OH$ where R^8 is hydrogen or lower alkyl and R^9 is lower alkylene;

Ar is phenyl; and

m, n, p and q are zero or integers from 50 to 10,000.

4. The membrane of claim 3, wherein the flexible connecting component is chosen from the group consisting of poly(alpha-olefins), polydienes, and hydrogenated derivatives of polydienes.

5. The membrane of claim 4, wherein the flexible connecting component is chosen from the group consisting of poly(ethylene-butylene) and poly(ethylene-propylene) and the ion-conducting domain is provided by a component chosen from the group consisting of the sulfonic acids of polystyrene and poly(α-methylstyrene), said membrane further characterized in that sulfonyl ester or sulfone crosslinking occurs between said polystyrene or

10   poly(α-methylstyrene) components.

      6.   A membrane according to claim 3, wherein
said membrane is an acrylonitrile-butadiene-styrene
terpolymer (ABS), the styrene component being
sulfonated.

      7.   A highly sulfonated polymeric membrane
produced by the process of:
            (a)   adding a 3-4 wt% solution containing
3.6 equivalents of styrene-(ethylene-butylene)-
5   styrene triblock copolymer in 80/20
dichloroethane/cyclohexane and a 3-4 wt% solution
containing about 3.6 equivalents of sulfur trioxide
in dichloroethane to a 0.6 wt% solution containing
about one equivalent of triethylphosphate in
10   dichloroethane at -5° to 0° C;
            (b)   stirring for 15 to 30 minutes at -5°
to 0° C, and then room temperature for 8 to 14 hours;
            (c)   heating at about 80° C for 30 to 40
minutes until a purple color is evident;
15   (d)   evaporating the dichloroethane and
cyclohexane at 40° C to obtain a viscous purple
liquid;
            (e)   resuspending the viscous purple liquid
to form a fine dispersion of 8 to 10 wt% in 80/20
20   dichloroethane/cyclohexane; and
            (f)   casting the dispersion on a substrate
to form a membrane that absorbs at least 50% of its
weight in water, that in its fully hydrated state can
be stretched to at least 100% of its original
25   dimension without fracture and that exhibits a
conductivity of at least 10^{-5} S/cm.

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     8.   A highly sulfonat d polymeric membrane
according to claim 7 wherein said styrene-(ethylene-
butylene)-styrene triblock copolymer has a number
average molecular weight of about 50,000 and wherein
5   styrene units comprise about 20 to 35 wt% of said
triblock copolymer.

     9.   A highly sulfonated polymeric membrane
according to claim 7 wherein said membrane is more
than 25 mol% sulfonated.

    10.   A fuel cell comprising: (a) the membrane of
any of claims 1 to 8; (b) first and second opposed
electrodes in contact with said membrane; (c) means
for supplying a fuel to said first electrode; and (d)
5   means for permitting an oxidant to contact said
second electrode.

    11.   A fuel cell according to claim 10 wherein
one of said first and second electrodes is composed
of catalytic particles and said membrane functions as
a binder for said electrode.

    12.   A process for preparing a mechanically
stable, ion-conducting membrane comprising the steps
of:
        (a)   adding a solution containing 3.6
5   equivalents of a styrene-containing block copolymer
in an appropriate solvent and a solution containing
about 0.9 to 3.6 equivalents of sulfur trioxide in an
appropriate solvent to a solution containing from
about 0.3 to about 1.2 equivalents of
10   triethylphosphate in an appropriate solvent at -5° to
0° C;

(b)   stirring for 15 to 30 minutes at -5°
to 0° C, and then room temperature for 8 to 14 hours;
(c)   heating at about 80° C until a color
change occurs;
(d)   evaporating the solvent to provide a
residue;
(e)   resuspending the residue to form a
fine dispersion in a suspending solvent; and
(f)   casting the dispersion on a substrate
to form said mechanically stable, ion-conducting
membrane.

13.   A process according to claim 12 wherein
said styrene-containing polymer is a styrene-
(ethylene-butylene)-styrene triblock copolymer having
a number average molecular weight of 50,000 and
wherein styrene units comprise about 30 to 35 wt% of
said triblock copolymer.

14.   A process according to claim 12 wherein
said membrane is more than 40 mol% sulfonated.

15.   A process according to claim 12 comprising;
(a)   adding a 3-4 wt% solution containing
3.6 equivalents of styrene-(ethylene-butylene)-
styrene triblock copolymer in 80/20
dichloroethane/cyclohexane and a 3-4 wt% solution
containing about 3.6 equivalents of sulfur trioxide
in dichloroethane to a 0.6 wt% solution containing
about one equivalent of triethylphosphate in
dichloroethane at -5° to 0° C;
(b)   stirring for 15 to 30 minutes at -5°
to 0° C, and then room temperature for 8 to 14 hours;
(c)   heating at about 80° C for 30 to 40
minutes until a purple color is evident;

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(d)   evaporating the dichloroethane and
15   cyclohexane at 40° C to obtain a viscous purple
liquid;

(e)   resuspending the viscous purple liquid
to form a fine dispersion of 8 to 10 wt% in 80/20
dichloroethane/cyclohexane; and
20   (f)   casting the dispersion on a substrate
to form said membrane.

16.   In a process for preparing a sulfonic acid
ionomer of a styrene-(ethylene-butylene)-styrene
triblock copolymer (SEBS), the improvement which
comprises using a sulfur trioxide-triethylphosphate
5   complex that is formed in the presence of the SEBS,
whereby said SEBS is not less than 25 mol%
sulfonated.

17.   An electrolysis cell comprising: (a) the
membrane of any of claims 1 to 8; (b) first and
second opposed electrodes in contact with said
membrane; (c) means for supplying a water to said
5   cell; and (d) means for withdrawing hydrogen and
oxygen from said first and second electrodes.

18.   An electrolysis cell according to claim 17
wherein one of said first and second electrodes is
composed of catalytic particles and said membrane
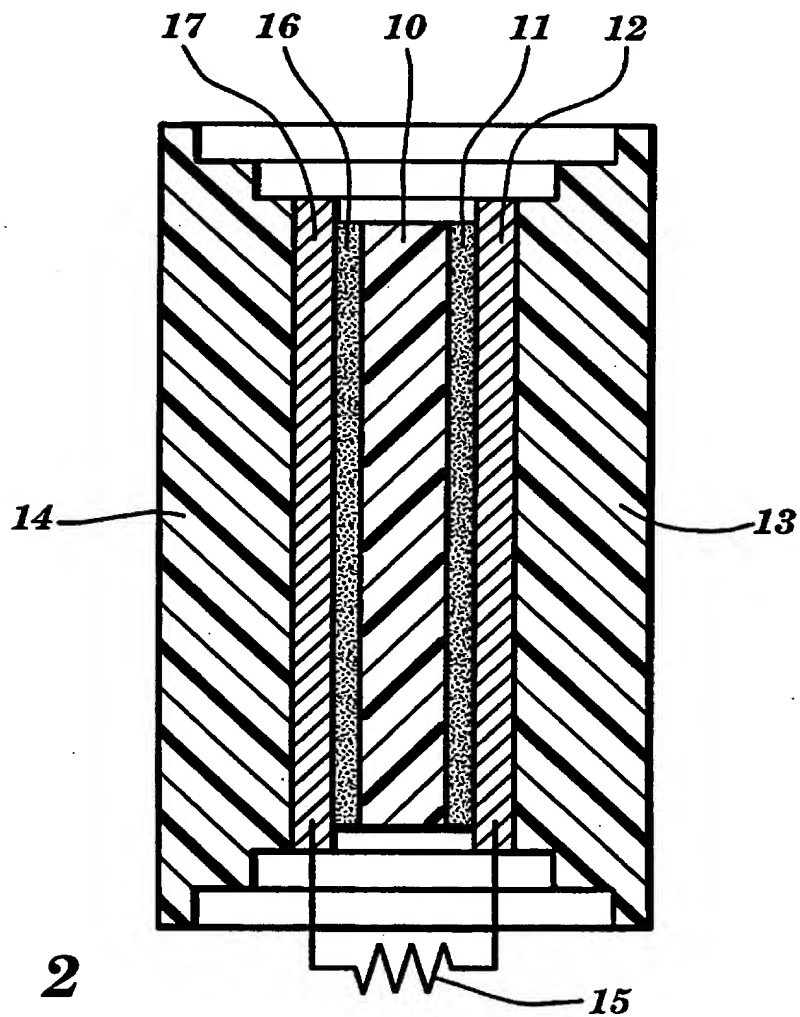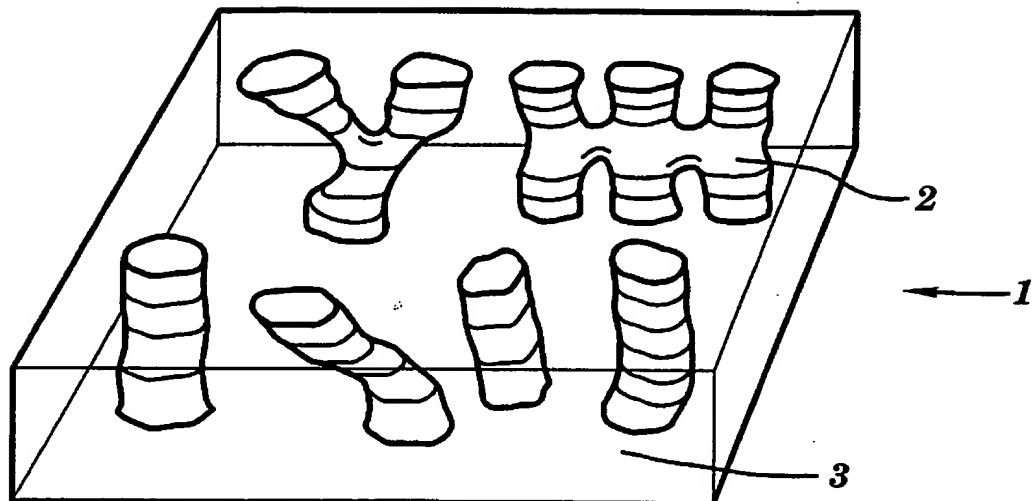functions as a binder for said electrode.

FIG. 1

FIG. 2

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6   C08J5/22   H01M8/10   H01M8/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   C08J   H01M   B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US-A-3 577 357 (WINKLER DE LOSS E) 4 May 1971 cited in the application see the whole document ---	1-5,12, 14
A	WO-A-87 07623 (ALLIED CORP) 17 December 1987 see page 5, line 2 - line 7; claims 1-12,24-27 see page 7, line 9 - page 8, line 24 see page 10, line 16 - line 31 --- -/--	1,3-5,12

[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 August 1995	0 5 -09- 1995

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Pamies Olle, S

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Section Ch, Week 7741 Derwent Publications Ltd., London, GB; Class A91, AN 77-73720Y & JP-B-52 036 997 (KUREHA KAGAKU KOGYO) , 19 September 1977 see abstract ---	1,3-5
A	MACROMOLECULES, vol. 21, 1988 US, pages 392-397, F.M. GRAY ET AL. 'NOVEL POLYMER ELECTROLYTES BASED ON ABA BLOCK COPOLYMERS' cited in the application see abstract ---	1,3
A	US-A-3 247 133 (WILLIAM KWO-WEI CHEN) 19 April 1966 see claims; example 3 -----	3,4

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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